Review

Constraints on nebular dynamics and chemistry based on observations of annealed magnesium silicate grains in comets and in disks surrounding Herbig Ae/Be stars

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Understanding dynamic conditions in the Solar Nebula is the key to prediction of the material to be found in comets. We suggest that a dynamic, large-scale circulation pattern brings processed dust and gas from the inner nebula back out into the region of cometesimal formation—extending possibly hundreds of astronomical units (AU) from the sun—and that the composition of comets is determined by a chemical reaction network closely coupled to the dynamic transport of dust and gas in the system. This scenario is supported by laboratory studies of Mg silicates and the astronomical data for comets and for protoplanetary disks associated with young stars, which demonstrate that annealing of nebular silicates must occur in conjunction with a large-scale circulation. Mass recycling of dust should have a significant effect on the chemical kinetics of the outer nebula by introducing reduced, gas-phase species produced in the higher temperature and pressure environment of the inner nebula, along with freshly processed grains with "clean" catalytic surfaces to the region of cometesimal formation. Because comets probably form throughout the lifetime of the Solar Nebula and processed (crystalline) grains are not immediately available for incorporation into the first generation of comets, an increasing fraction of dust incorporated into a growing comet should be crystalline olivine and this fraction can serve as a crude chronometer of the relative ages of comets. The formation and evolution of key organic and biogenic molecules in comets are potentially of great consequence to astrobiology.

Comets: Ancestors and Antecedents of the Solar System

It is almost an article of faith among members of the planetary science community that comets are the most primitive bodies in the Solar System. In general, this is taken to mean that materials in comets are preserved in nearly the same state today as when the material originally aggregated from the Solar Nebula to form cometesimals. Nothing we say below will contradict this axiom. However, we will show that comets are not simply collections of unaltered presolar grains and ices formed in the precollapse molecular cloud, but are instead aggregates of materials representative of the building blocks then present in the nebula at the time of their accretion. In our opinion, comets represent the best grab bag samples of material from the primitive Solar Nebula. However, this does not imply that materials incorporated into cometesimals did not undergo very significant processing in the nebula itself, only that little further processing occurred once material was incorporated into the cometesimal.

In this paper, we show that grains incorporated into comets and seen around young A and B stars as their protoplanetary disks begin to clear contain silicate grains that have undergone processing at temperatures as high as 1,100 K for periods of minutes, or more likely, at temperatures near 1,000 K for days to weeks, and that such processing can only have occurred in the inner nebula. After processing, the grains were transported beyond the protostellar snow line where they acquired a primarily water-ice mantle, and became part of freshly accreted cometesimals. In the following sections, we briefly discuss observations of young, 2–3 solar mass stars as analogs of solar-mass systems, and review UV observations that establish the presence of significant cometary infall rates in the disks of young A- and B-stars. We then discuss laboratory evidence detailing the IR spectral evolution of amorphous magnesium silicate dust subjected to thermal annealing. We show that the IR spectra of dust in these stars changes systematically with the age of the star and that dust around older stars contains higher fractions of processed material than does the dust surrounding younger A-stars.

This evidence implies that dust (and gas) mixing and transport scales in protostellar nebulae could be many tens to several hundred AU and that such enormous mixing lengths could have significant consequences for nebular chemistry. We argue that dust and volatiles in comets should be reflective of the period in nebular history during which an individual comet aggregated. Therefore, because the spectral properties of the dust available for accretion evolves with time, the spectral properties of the dust can be used to establish a cometary age sequence. Comets formed early in nebular history will contain only primitive, amorphous interstellar grains and ices because no nebular processing has had time to occur. Comets formed very late in nebular history will contain considerably more crystalline olivine dust and complex organic materials. These complex organic molecules could have played an important role in the origin of life on Earth and possibly on other bodies throughout the Solar System. Indeed, they could represent a natural, primary process occurring in every protoplanetary system.

A-Stars: Astronomical Laboratories for Studying Comet Infall

Our goal is to understand conditions in the Solar Nebula at the epoch of planetesimal formation and planet building. This goal can be approached by studies of the fossil record—the comets, or meteorites—and by observations of stars with protoplanetary disks of the desired age. Studies of circumstellar material associated with young solar-mass stars are hampered by strong stellar activity, and

Abbreviation: AU, astronomical unit.

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low relative luminosity of the stars. Slightly more massive stars (2–3 solar masses), Herbig Ae/Be stars, are surrounded by significant dust disks (1–3) with diameters comparable to or somewhat larger than the diameters of disks observed around lower-mass stars (4). The disk evolutionary time scales, measured by the presence of a near-IR excess and optical emission signatures, appear comparable to young solar-type stars (5), suggesting that the time required to clear the inner few AU of the disks are also comparable. Observations suggest that IR excesses associated with colder, and hence more distant, material in the disks drop gradually with age for single stars, and become undetectable by 400 million years ago (Myr) (6), which is compatible with the duration of the heavy bombardment phase in the inner Solar System. Because of the higher effective temperatures (7,500–10,500 K) of these stars, they have both higher UV luminosities and relatively simple stellar spectra compared with young solar-type stars, making them convenient laboratories for probing the evolution of protoplanetary nebula.

The first indication that such systems might harbor comets came from the nearby [d = 19.6 pc (parsec = 3.09×10^{16} m)] A-star β Pictoris (7), which is surrounded by an extensive dust disk (8). Replenishment of μm-sized dust in the disk of this 20 million-year-old star (9) requires a population of larger bodies (10). Similar conclusions have been reached from the study of circumstellar absorption features that are conspicuous in the UV and optical spectrum of β Pictoris. Shortly after detection of the disk, UV spectroscopy of the star revealed circumstellar absorption features that are systematically red-shifted (11–13). The time-variable nature of these red-shifted absorption features suggest that they occur following planetary perturbation of swarms of comets resident in the disk (13–15). As these comets fall toward the central star, the volatiles evaporate and appear to an outside observer as red-shifted absorptions. For a more complete discussion, see ref. 16.

Similar, red-shifted, gas-phase absorption features are observed in many Herbig Ae/Be stars (17, 18). Such stars are thought to be younger than β Pictoris (19, 20), spanning the range from premain sequence (PMS) to zero-age main sequence (ZAMS). For the youngest stars, the composition of the infalling gas is comparable with unprocessed disk material (21) and is routinely observed, in contrast to the episodic nature of the infall in β Pictoris (18). For some older Herbig Ae/Be stars, the infall activity is either episodic (22) or deviates from the stellar composition, suggesting that in these cases, infall of processed material is being witnessed.

Observations of Stellar Winds

Herbig Ae/Be stars, like young solar-type stars, have strong stellar winds that have been identified from their optical (23–25) and UV spectra (17, 26) (Fig. 1). Winds typically have radial velocities of 200–400 km/s, and are more easily observed in systems where material from the disk does not obscure the star (17). The precise geometry of these winds has been a topic of lively discussion. Recent Hubble Space Telescope (HST) observations indicate that in at least one case (HD 163296) the outflow consists of two spatially distinct components: (*i*) a collimated, bipolar outflow moving with space velocities of 300–500 km/s (27); and (*ii*) an apparently uncollimated flow, detectable in scattered Lyman alpha up to 1.5″ (180 AU) from the star. The presence of the collimated outflow, together with FUV emission features compatible with the presence of a chromosphere/transition region, suggests that many of the same mechanisms thought to be active in the young Solar System may also be effective in these protoplanetary disks. It is the uncollimated outflow, if typical of young stars, that can potentially provide a mechanism for cycling material from the inner disk out to distances of tens to hundreds of AU where cometesimals can begin to form.

Evolution of Silicate Spectra: Laboratory and Astrophysical Comparisons

The IR spectra of silicates in the interstellar medium and around most Asymtotic Giant Branch (AGB) stars show that they are

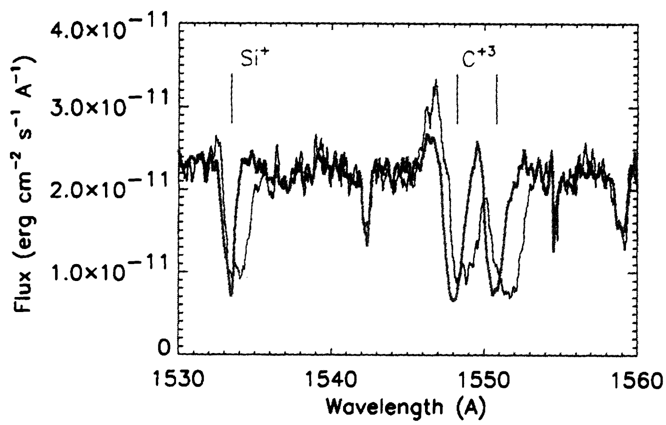

Fig. 1. UV spectra obtained with the IUE of the Herbig Be star HD 100546 at two epochs (thin and thick lines). The spectra illustrate variability in the red-shifted infall features and variability in the strength of blue-shifted absorption associated with the stellar wind. The wind can be traced to ≈200 km/s. The electronic transitions involved are the Si^{+} UV multiplet 2 and the resonance doublet of C^{+3}.

amorphous and characterized by a broad, relatively featureless pair of infrared peaks at ≈9.7 and ≈20 microns. Although recent observational evidence has shown that a fraction (≈10%) of the silicate formed around the highest-mass-loss-rate AGB stellar population is actually crystalline (28, 29), it is unlikely that crystalline grains comprise a significant fraction of interstellar silicates. Even if crystalline silicates escape destruction via supernova shock waves (30, 31), their crystallinity will be destroyed via long exposure to galactic cosmic rays (32). Therefore, the silicate dust observed around most premain sequence (PMS) stars should be amorphous.

If we examine the IR spectra of Herbig Ae/Be stars, we find a mixture of dust types, including highly amorphous silicates akin to interstellar silicates and to glass with embedded metal sulfide (GEMS) within interplanetary dust particles.‖ We also find reasonably well crystallized materials (16, 19, 34, 35). The most conspicuous examples of crystallized materials are seen in the Herbig Ae/Be stars that are either near the zero-age main sequence (ZAMS) and/or exhibit IR excesses suggestive of significant clearing of the inner disk (30, 36–40), including HD 100546, where the silicate emission bands are indistinguishable from those seen in comet Hale-Bopp. Younger and/or less centrally cleared Herbig Ae/Be stars tend to show stronger amorphous silicate emission (16, 41–43).

This trend prompted Waelkens *et al.* (34) and Nuth‖ to suggest that the silicate crystallinity should increase with stellar age due to processes occurring within the circumstellar disk. The presence of amorphous silicates resembling interstellar grains and the presence of GEMS in interplanetary dust particles effectively eliminates dust processing via an accretion shock as the source of the crystalline material seen in older nebulae. Though Molster *et al.* (45) argued for low temperature crystallization of dust in higher density regions of disks (based on detection of similar silicate bands in circumstellar material associated with evolved stars that are in the process of building planetary nebulae), no mechanism for such crystallization has been proposed. In contrast, laboratory annealing studies of Mg silicates summarized below provide constraints on the temperature and time required to transform amorphous, circumstellar/interstellar silicate dust into crystalline grains.

Hallenbeck *et al.* (46) published a study of the evolution of amorphous magnesium silicate smokes subjected to thermal annealing *in vacuo* at temperatures near 1,000 K. The rate of

‖Nuth, J. A., Lunar and Planetary Science Conference, March 15–19, 1999, Houston, TX, abstr.

Table 1. Time required to crystallize amorphous silicates

Annealing temperature (K)	Time to crystallization
1,100	1.9 s
1,050	1.13 h
1,000	220 days
950	6976 years
900	225 million years
850	2,441 billion years

evolution of the spectrum of silicates is extremely sensitive to the temperatures to which they are exposed. A more recent study can be used to predict the IR spectrum of grains annealed at any given temperature and time (47). Whereas magnesium silicate smokes anneal beyond the stall (46) in only ≈2 h at 1,048 K, at 1,000 K this same transition requires ≈300 days. Annealing small interstellar silicates at significantly higher temperatures (e.g., $T > 1{,}500$ K) could result in their vaporization, whereas annealing at lower temperatures could require millions of years to achieve significant changes (Table 1), and thus cannot be the source of crystalline silicates in young Herbig Ae/Be stars. Malfait *et al.* (36) demonstrated the similarity of the dust spectrum for HD 100546 (t = 10 million years) to dust in comet Hale-Bopp, and Knacke *et al.* (48) have suggested similarities between dust in the β Pictoris system and that seen in olivine-rich comets. More recent observations (49) suggest that dust in this system is a mixture of amorphous silicates and only a small fraction of crystalline grains. Because dust around β Pictoris, and potentially also around HD 100546 (22) most likely originates in evaporating comets, the dust in those comets must have been processed at high temperatures—on the order of 1,000 K. And because Comets Halley, Hale-Bopp, Bradfield, and Mueller also exhibit olivine-rich dust features (50), one can infer that some dust in these comets was also exposed to high temperatures before incorporation into the individual comet. Hallenbeck *et al.* (46) demonstrated that dust spectra of these comets can be fit by using the same set of IR peaks used to fit the spectra of partially annealed magnesium silicate smokes in the laboratory (Fig. 2). Given the similarity of the laboratory spectra to those in comets, we believe that we understand the degree of annealing required in the natural system to reproduce the observations. Such temperatures (≈1,000 K) are only found within the innermost regions of the solar and other protoplanetary nebulae (51).

Chemistry of Protostellar Nebulae

Our understanding of chemical processes in the primitive Solar Nebula and of processes common to nebulae surrounding many protostars, has increased considerably as more detailed models of nebular evolution have become available. Early models (52) simply assumed that very hot gas in the Solar Nebula cooled slowly enough to maintain thermodynamic equilibrium until at least the more refractory vapors had condensed. Later models (53) examined potential consequences of local to medium-scale turbulence that would naturally accompany any viscous accretion disk. Prinn and Fegley (54) demonstrated that even major gas phase species such as N_2/NH_3 could fail to achieve equilibrium because of low temperatures and slow chemical-reaction rates near the outer planets. More recent work (55) has demonstrated that, for mineral species, constraints in achieving equilibrium with gas in the nebula are even

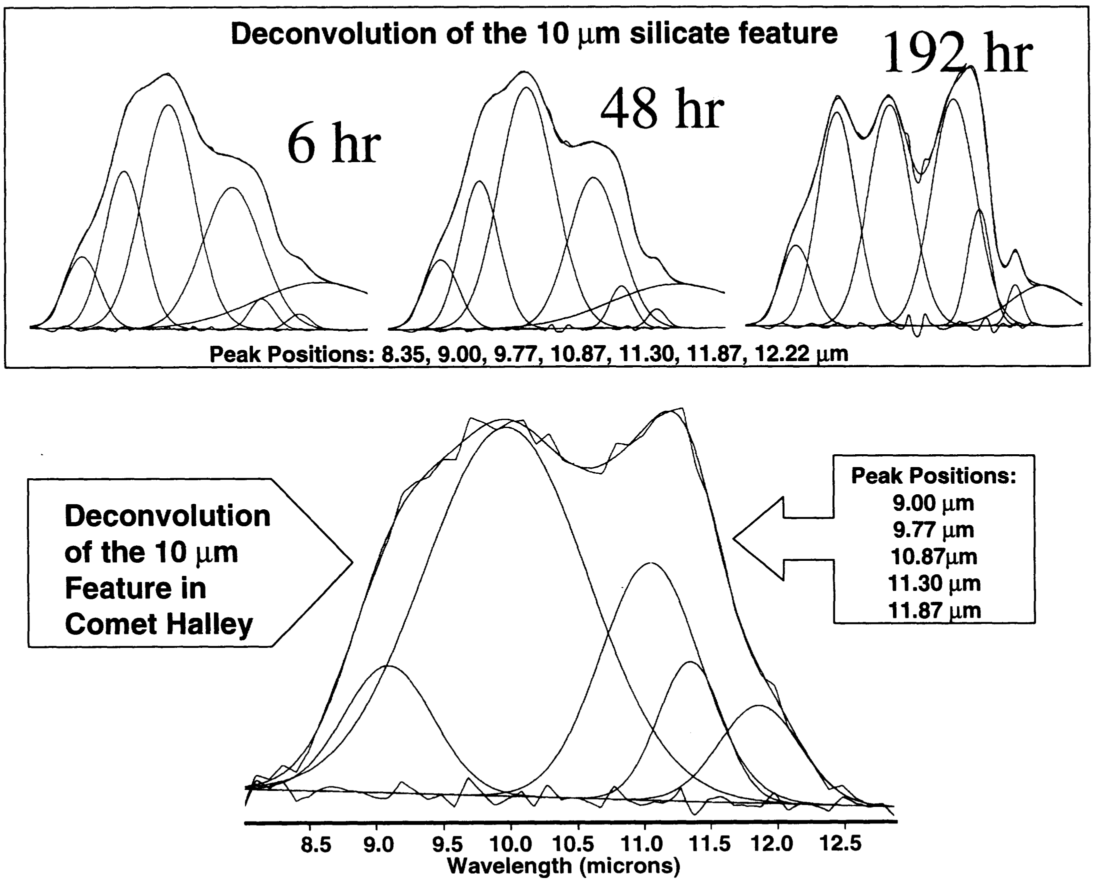

Fig. 2. Three IR spectra (*Upper*) of amorphous Mg silicate smoke annealed in the laboratory for 6, 48, and 196 h at 1,027 K, fit by using seven gausian peaks and compared with the spectrum of dust in comet Halley, fit by using five of these same peaks.

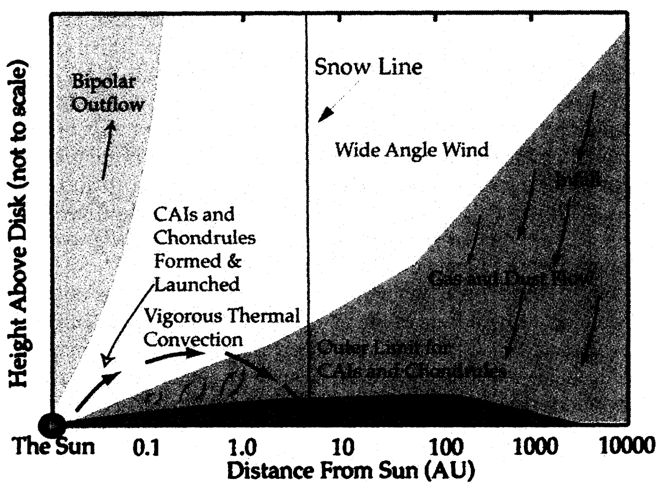

Fig. 3. Schematic drawing of a protostellar nebula (distance on a log scale) centered on the protoSun. The region of dust processing is shown (<1 AU) together with the snow line (≈5 AU), infalling envelope, bipolar outflow, and less collimated wind. Comet formation is expected to occur from ≈5 to beyond 40 AU.

more severe. In particular, oxidation/reduction or hydration reactions expected to occur spontaneously at temperatures ranging from 500 K to 700 K might easily lack the time necessary to achieve equilibrium in a rapidly evolving Solar Nebula.

Observations of Herbig Ae/Be stars discussed above add to the difficulties of assuming that chemical equilibrium is ever achieved at any place or time in the evolution of protostellar nebulae. Most models assume that mass accretion onto the sun occurs in a predictable way: mass falls onto the accretion disk and travels more or less steadily inward. Even turbulent mixing scenarios (53) are primarily consistent with this picture, because mixing only really occurs between adjacent chemical regimes. Observation of a large population of annealed silicates in comets perturbed into star-grazing orbits following planetary encounters implies that mixing occurs on significant distance scales. Such scales (several AU to ≫ 100 AU) far exceed those in the models (53). This is consistent with the constraint that thermal annealing at ≈1,000 K must be followed by condensation of an ice mantle onto annealed grains before their aggregation into comets. In a simple-minded scenario, mixing occurs from an annulus within about 1 AU from the central star out to well beyond at least 5 to 10 AU. In reality, the mixing lengths are probably both much longer and shorter than this (Fig. 3).

Shu *et al.* (56, 57) suggested that grains and dust aggregates reaching the surface of the protosun, in contact with the accretion disk, could be hurled out along magnetic field lines to land in the region of chondrite formation. Grains reaching such temperatures as part of a large dust aggregate quickly melt and coalesce through surface tension (greatly reducing their exposed surface) and resist evaporation until transported to cooler environments. Individual 10- to 100-nm grains exposed to solar surface temperatures would rapidly vaporize. Even if such vapors later recondensed, the new silicates would be highly amorphous and their IR spectra would more resemble grains condensed around the majority of mass-losing Asymtotic Giant Branch (AGB) stars than grains from olivine-rich comets. It seems unlikely that the chondrule-forming mechanism of Shu *et al.* (57) is directly responsible for transporting individual submicron grains heated to more moderate temperatures (≈1,000 K) to the outer nebula.

Large-scale circulation patterns that are capable of transporting significant quantities of presolar silicates from hotter nebular environments to beyond the snow line must exist at some stage of nebular evolution. Because individual grains should be closely coupled to the gas, such circulation patterns would also transport an even larger mass of gas equilibrated at high temperatures (≈1,000 K) out beyond the giant planet formation region. The gas composition would be similar to that predicted for Giant Gaseous Protoplanetary Subnebulae (58, 59), but would probably be spread more uniformly around the accretion disk.

If there is a steady flow from the inner to the outer regions of the Solar Nebula, then the chemistry of the gas-phase would be dominated by chemical kinetics to a much greater degree than currently modeled (54, 55). In particular, circulation patterns could lead to freshly condensed and partially annealed grains (natural, catalytic surfaces) in the outer Solar System. This could greatly enhance rates of gas-grain reactions, such as the Fischer Tropsch-Type synthesis of methane and higher hydrocarbons from CO and H_2 or the analogous conversion of molecular N_2 and H_2 to NH_3 (61, **). Such catalytic syntheses would be over and above the NH_3 and hydrocarbons produced in the inner Solar System and transported with the processed grains.

The dynamic circulation pattern suggested by the steady increase in the proportion of processed dust in comets around Herbig Ae and Be stars is not consistent with models of evolving stellar accretion disks. This inconsistency may be due more to the limits of computational techniques used to model angular momentum transport in disks than to any physical reason preventing such circulation. In fact, large-scale circulation cells moving material from the inner to the outer regions, both above and below an inward-flowing accretion disk, have been discussed by both Prinn (62) and Stevenson (63). Perhaps it is time to reconsider this topic, at least for its potential to accurately predict the chemistry of comets.

The Formation of Comets

Weidenschilling (64) examined the formation of comets in a minimum mass nebula by using a one-dimensional model to follow accretion of μm-sized dust particles into kilometer-scale bodies. Comets form on time scales of a few hundred thousand years, even neglecting action of several factors that result in swifter accretion rates. A growing comet accretes material from a large volume in the nebula; the initial coagulation process is aided greatly by gas-drag-induced orbital migration. Migration homogenizes material accreted into comets by giving them feeding zones from 10 to 100 AU in radius that obscure small compositional differences between comets that end up at different nebular radii. Comets form much more rapidly in higher mass nebulae where gas-drag-induced orbital migration and accumulation due to gravitational instabilities would be more important. The differences we might expect to observe in the dust and volatile compositions of individual comets depends on the ratio of comet accumulation time scale to nebular lifetime. If these are comparable, then all comets look similar. If the nebular lifetime were much longer than the time required to accumulate comets, then substantial diversity will exist in this population as the crystalline fraction of the dust and the complex organic content of the volatiles increases with time. These latter predictions certainly appear to be more consistent with observations of both the dust (50, 65) and gas (66, 67) content of recent comets.

Comets formed early in nebular history will consist of amorphous silicates and unaltered interstellar ices; no processed material is yet available. Comets formed late contain more hydrocarbons, ammonia, and annealed dust than those formed earlier. This increase will not necessarily be linear. However, after accretion of fresh material from the surrounding molecular cloud ceases, accumulation of processed gas and dust in the comet formation region should at least be monotonic. The time-dependent nature of dust and gas accreted into comets might easily obscure less significant differences in cometary chemistry such as potential distinctions between comets accreted

Fegley, B. (1998) *Bull. Am. Astron. Soc.* **30, 1092 (abstr.).

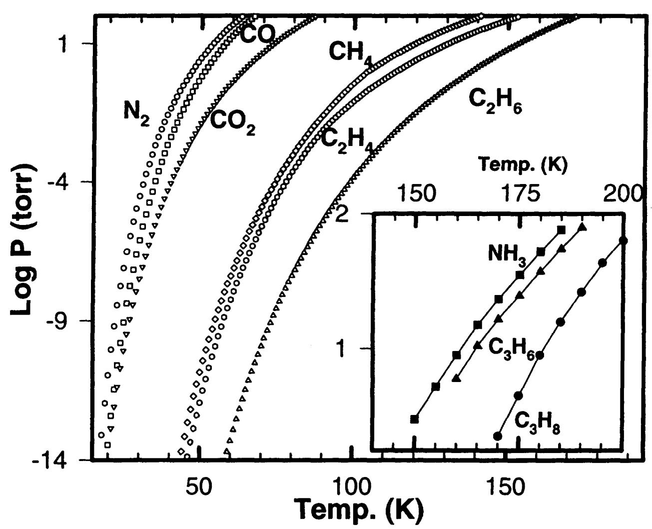

Fig. 4. Calculated and empirical vapor pressures in the range 15–200 K (68, 69). Compounds include interstellar grain mantle (N_2, CO, CO_2) and hydrogenated nebular species (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, NH_3). C_2H_6, C_3H_8, and NH_3 are enlarged for clarity.

at higher temperatures in the Jupiter–Saturn region and those accreted in cooler zones near, or even beyond, Uranus–Neptune.

Older comets should be rich in CO, CO_2, N_2, and amorphous dust, whereas younger comets contain an abundance of crystalline olivine, hydrocarbons, NH_3, and prebiotic organics. We predict that the fraction of crystalline dust is correlated to the ratios of hydrocarbons to CO and of NH_3/amines/amides to N_2. Fig. 4 shows vapor pressures (68, 69) for compounds formed in molecular clouds, present as icy mantles on interstellar grains (N_2, CO, and CO_2) along with more hydrogenated species synthesized in the nebula (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and NH_3). Interstellar grains heated above $\approx$50 K lose CO and N_2 from their mantles, whereas interstellar CO_2 could remain trapped. Hence, CO and N_2 are both suitable indicators of interstellar volatiles in comets. Alternatively, if NH_3 and most hydrocarbons synthesized in the nebula are cooled below $\approx$150 K, they will be trapped on grain surfaces. CH_4 requires much cooler temperatures to achieve the same degree of condensation and might not condense into comets even if it were present in the nebula. Therefore, CH_4 would not make a useful indicator of processed nebular gas in comets. One good proxy for the ratio of the processed-to-primitive nebular gas in comets is the ratio of C_2H_4 to CO, another is the ratio of C_2H_6 to CO. Hydrocarbons are synthesized primarily in the nebula and thereafter trapped on icy grains, whereas CO is associated with grain mantles formed within a giant molecular cloud core that had never been sufficiently heated to permit vaporization. Using similar reasoning, the ratio of NH_3 to N_2 should also be a good measure of the ratio of processed-to-primitive gas in comets. Hence, the ratio of crystalline (to total) cometary dust will be positively correlated to ratios of C_2H_4/CO, C_2H_6/CO, and NH_3/N_2 in cometary comae.

Implications for Astrobiology

Prebiotic synthesis of biogenic molecules has traditionally been viewed as a planetary process. Unfortunately, the classic Miller–Urey Experiment (70, 71) requires a reducing atmosphere to efficiently synthesize amino acids and the early terrestrial atmosphere was at best just slightly oxidizing, consisting largely of N_2 and CO rather than the CH_4, NH_3, and H_2O that Urey originally hypothesized. Modern assessments are even more pessimistic for the abiotic synthesis of organic materials as CO_2 may have been a major atmospheric constituent (72–74). Several workers (75, 76) pointed out that such an atmosphere makes abiotic synthesis of amino acids difficult to explain. Miller (77) asserted that although methane is the primary source of amino acid production, it can still occur when using CO and CO_2. Clearly the latter are less favored than CH_4 for amino acid synthesis, but may have contributed adequately. Undersea vents are now an integral part of the new Astrobiology Program. Such vents are reducing environments that might produce prebiotic organics on the primitive earth and might also exist on other planetary bodies such as Europa. However, these vents are not the only source of biogenic compounds available throughout the primitive Solar System.

Comets have been invoked as a source of organic materials needed for the evolution of life on Earth (78), and this idea has been revived recently (79). Comets are interesting because they may have delivered large volumes of water, along with the organics. Biogenic compounds like amino acids have not been identified in comets, but comets do contain simple volatile organic compounds, CH_3OH, H_2CO (68), C_2H_2 (80), C_2H_6 and CH_4 (81), and H_2CO_2. Volatiles are observed in cometary comae. Laboratory experiments show that other organic compounds form from these molecules with an appropriate energy source, such as ion-bombardment or UV-irradiation. The overall suite of complex organics in comets is still unknown and may remain so until examined by a cometary lander. *In situ* sampling and sample return missions will be very important because large amino acids and primitive proteins are less volatile than water and would remain in the nucleus to temperatures well above 300 K.

The sources of organic materials in comets are unknown. They could represent unmelted, unprocessed ices and organic residues on presolar interstellar grains. Additional components may be low molecular weight organics synthesized in the nebula, or in higher pressure subnebulae of the giant planets. These hypotheses have been studied and both have had some success in explaining volatiles in comets (55). Gas-grain reaction experiments appropriate for such environments are in their infancy (82) and must be extended by using more realistic catalytic materials. Another new avenue for research is coupled accretion, chemistry, and dynamic evolution of planetesimals. Trapped radicals from presolar ices could react with liquid water in the interior of water-rich planetesimals subject to radioactive heating to form amino acids. Liquid water was present in many planetesimals and left an extensive record of hydrothermal alteration easily read in the meteoritic record. Water was also present on the early Earth and reaction of radicals produced via space irradiation of organics could occur following the fall of an icy planetesimal into a lake or pond.

A second aspect of this problem is the delivery of the organics, intact, to the primitive Earth. However, meteorites deliver a considerable quantity of organic material to the modern Earth each year. Some very fragile meteorites have survived passage through the atmosphere, as have meteorites containing a significant (>10%) mass of organics (83). Fragile organic components are preserved within the frozen bolide because of the inefficient transfer of thermal energy to the interior and heat dissipation by sublimation of its outer layers. If cometary ices are at least as coherent as the more fragile meteoritic specimens found in our museums, and if entry heating ablates the surface rather than conducting heat into the interior, then solid pieces of cometary ice could fall into primitive lakes or oceans. Recent studies (44, 84, ††) have shown that significant fractions of amino acids in icy impactors survive to planetary surfaces. Infalling material could have had a considerable effect on the organic chemistry of the early oceans, as some models predict that a significant fraction of the Earth's oceans were acquired from c-type asteroids and comets (79).

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Though comets do contain volatile organic compounds, their overall complement of organics is completely unknown. Even the volatile compounds detected by ground-based observational studies are not easily predictable by standard models of nebular chemistry (55). Most models invoke a combination of nebular processing and chemistry in the higher temperature–pressure environments of Giant Gaseous Protoplanets to explain observed ratios of reduced/oxidized cometary molecules (e.g., NH_3/N_2 or C_nH_{2n+2}/CO). Studies of catalytic activity on interstellar grain surfaces or on grains formed *in situ* are just beginning (62, 82, **). Much more work is needed to extend the work of Anders on Fischer–Tropsch-type reactions in the nebula (60).

Understanding the dynamic conditions in the Solar Nebula is key to successful prediction of the material found in comets. If gas and grains formed in cold molecular clouds take a one-way trip into the sun then comets will be dominated by interstellar species sparsely leavened with molecules that formed in Giant Gaseous Protoplanets. If there is large-scale circulation bringing processed dust and gas from the inner nebula back out into the region of comet formation, then the composition of comets will be determined by a chemical–kinetic reaction network closely coupled to the dynamic transport of dust and gas in the system (85). It is impossible to predict the output of this chemical reaction network without a comprehensive understanding of the dynamics of the nebula. Unfortunately, current models of protostellar nebulae are far from ready to supply the detailed environmental and dynamic parameters needed to construct a complete model. Without such a model, understanding chemical evolution leading to the origin of life on Earth and in the Solar System is an unconstrained problem with little prospect for a unique solution. As such, it is imperative that detailed models of the dynamics of protostellar nebulae and appropriate observational programs to test and constrain them must be accorded high priority by astrobiologists.

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